

# Manganese-Catalyzed Highly Selective Oxidation of Hydrosilanes to Silanols under Neutral Conditions

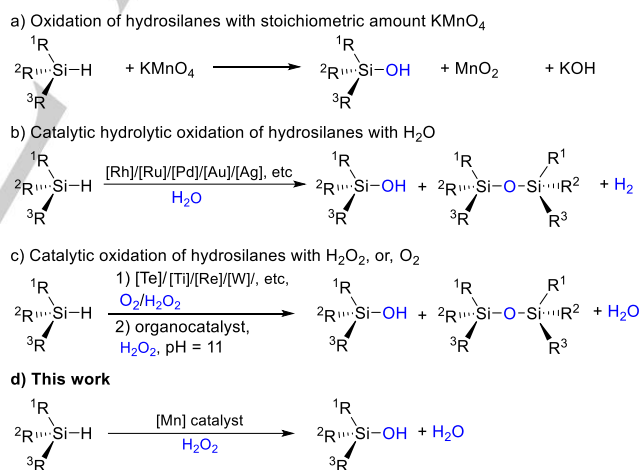
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**Abstract:** The first manganese-catalyzed oxidation of organosilanes to silanols with H<sub>2</sub>O<sub>2</sub> under neutral conditions has been accomplished. A variety of organosilanes with alkyl, aryl, alkynyl, and heterocyclic substituents were tolerated, so were sterically hindered organosilanes. The oxidation appears to proceed via a concerted process involving a manganese hydroperoxide species. Featuring mild conditions, fast oxidation and no waste byproduct, the protocol allows for a low-cost, eco-benign synthesis of both silanols and silandiol.

Silanols have found broad applications as monomers for silicon-based polymers,<sup>[1,2]</sup> functional groups of drugs,<sup>[1,3]</sup> directing groups for C-H functionalization,<sup>[1,4]</sup> donors for metal-catalyzed coupling reactions,<sup>[1,5]</sup> and organocatalysts<sup>[1,6]</sup> (see Figure S1 in Supporting Information). Whilst less bulky silanols can be synthesized by hydrolysis of chlorosilanes under strictly controlled conditions, it is difficult to synthesize sterically hindered silanols, silandiol, and silanols with functional group sensitive to hydrolytic conditions.<sup>[1,7]</sup> Silanols can also be synthesized by oxidation of organosilanes<sup>[1a,1b]</sup> with strong oxidants, such as silver salts,<sup>[8a]</sup> permanganate,<sup>[8b]</sup> osmium tetroxide,<sup>[8c]</sup> dioxiranes,<sup>[8d]</sup> peracids,<sup>[8e]</sup> oxaziridines<sup>[8f]</sup> and ozone.<sup>[8g,8h]</sup> Apart from generating stoichiometric amounts of waste, these methods are often accompanied with problems of selectivity, e.g. producing undesired siloxanes via condensation of two molecular silanols, or byproducts due to silanol decomposition.<sup>[8]</sup> For example, in the oxidation of organosilanes with permanganate, silanols and silandiol were obtained with poor selectivity in addition to the formation of wasteful MnO<sub>2</sub> (Scheme 1a).<sup>[8b]</sup> Furthermore, as the reaction condition is basic, base-catalyzed rearrangement can take place.<sup>[8b]</sup> Catalytic oxidation of Si-H bonds with a clean oxidant and high selectivity is still a challenge.

Noble metal catalysts, e.g. those based on Rh,<sup>[9a]</sup> Cu,<sup>[9b]</sup> Re,<sup>[9c]</sup> Ru,<sup>[9d]</sup> Pd,<sup>[9e]</sup> Ir,<sup>[9f]</sup> Au,<sup>[9g-i]</sup> and Ag,<sup>[9j,9k]</sup> have been demonstrated to promote efficient oxidation of hydrosilanes to silanols with hydrogen gas formation. However, such hydrolytic oxidation cannot completely avoid the formation of disiloxane by-products,

because the silanol product itself may react with the hydrosilane (Scheme 1b).<sup>[9,1a]</sup> Whilst water is an ideal oxidant, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> are also cheap and environmentally friendly in comparison with other stoichiometric oxidants.<sup>[8]</sup> A few catalysts based on Ti,<sup>[10a,10b]</sup> Re,<sup>[10c,10d]</sup> Te,<sup>[10e]</sup> and W<sup>[10f]</sup> have been explored for the oxidation of hydrosilanes by using H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> as oxidant. Disiloxanes were also formed with these catalysts, however (Scheme 1c).<sup>[10]</sup> More recently, trifluoroacetophenone was reported to catalyze the oxidation of hydrosilanes with H<sub>2</sub>O<sub>2</sub>, affording a series of silanols with excellent yield and selectivity, but requiring strictly pH-controlled buffer conditions (Scheme 1c).<sup>[11]</sup> Clearly, although transition metal-catalyzed hydrolytic oxidation and oxidation with H<sub>2</sub>O<sub>2</sub> now allow for the oxidation of hydrosilane to silanols, few of the reported catalytic systems can avoid the formation of disiloxane or other by-products. Therefore, it remains valuable to develop a more efficient catalytic system that features a cheap, environment friendly catalyst and operates under neutral conditions for the oxidation of organosilanes to silanols.



**Scheme 1.** Synthesis of silanols by oxidation of hydrosilanes.

Whilst manganese-catalyzed oxidation with H<sub>2</sub>O<sub>2</sub> of C=C and C(sp<sup>3</sup>)-H bonds has been studied extensively, no examples of the oxidation of organosilanes with a manganese catalyst have ever been reported.<sup>[12]</sup> Owing to the importance of silanols and our interest in catalytic oxidation,<sup>[13]</sup> we thought it would be interesting to develop a more selective catalytic system based on cheap, eco-benign manganese as catalyst and H<sub>2</sub>O<sub>2</sub> as oxidant for the oxidation of organosilanes (Scheme 1d). Initially, we chose dimethyl(phenyl)silane **2a** as the model substrate to identify possible catalyst for the oxidation with H<sub>2</sub>O<sub>2</sub> in an acetone medium. We quickly found that the simple manganese salt, Mn(ClO<sub>4</sub>)<sub>6</sub>·6H<sub>2</sub>O (5 mol%), had no catalytic activity for the target transformation (entry 1, Table 1). The introduction of

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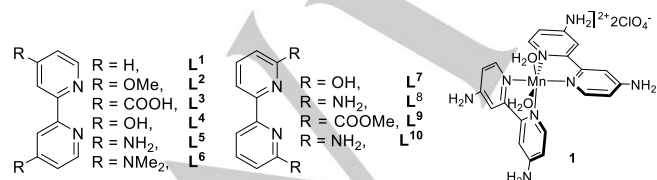
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nitrogen ligands brought about changes. Thus, on combining bipyridine **L**<sup>1</sup> (10 mol%) with Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (5 mol%), silanol **3a** was formed in 6% GC yield (entry 2, Table 1). We then explored the electronic effect of ligand by using a range of 4,4'-disubstituted bipyridines (**L**<sup>1</sup>–**L**<sup>6</sup>) and observed, remarkably, that the electron-rich 4,4'-diamino bipyridine **L**<sup>5</sup> enabled an almost full oxidation of **2a** to **3a** with no formation of the disiloxane byproduct (entries 2–7, Table 1). In sharp contrast, the electron-deficient **L**<sup>3</sup> is ineffective. The steric effect is equally critical, as changing the ligand to 6,6'-disubstituted bipyridines brought about little oxidation of **2a** (entries 8–11, Table 1). Further screening of other ligands as well as the combination of **L**<sup>5</sup> with other manganese or iron salts demonstrated that **L**<sup>5</sup> combined with Mn(ClO<sub>4</sub>)<sub>2</sub> exhibits the best catalytic activity in the oxidation of **2a** with H<sub>2</sub>O<sub>2</sub> (Table A, SI). The catalyst loading could be lowered from 5 mol% to 1 mol% without affecting the yield of **3a** (entry 13, Table 1); but in the absence of Mn(ClO<sub>4</sub>)<sub>2</sub>, no reaction was observed (entry 12, Table 1).

**Table 1.** Oxidation of dimethyl(phenyl)silane with H<sub>2</sub>O<sub>2</sub> catalyzed by manganese catalysts<sup>a</sup>

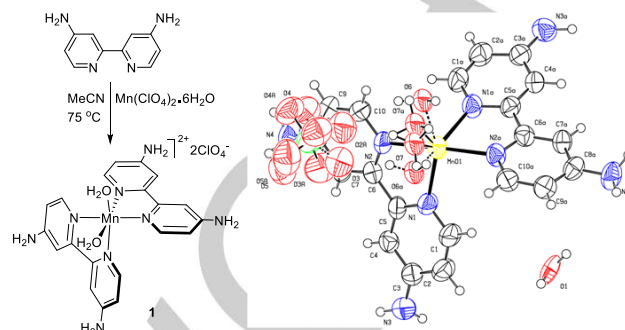
Entry	Ligand	Manganese salt or complex <b>1</b>	Solvent	Yield of <b>3a</b> (%)
1	none	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	0
2	<b>L</b> <sup>1</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	6
3	<b>L</b> <sup>2</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	11
4	<b>L</b> <sup>3</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	trace
5	<b>L</b> <sup>4</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	26
6	<b>L</b> <sup>5</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	99
7	<b>L</b> <sup>6</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	75
8	<b>L</b> <sup>7</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	trace
9	<b>L</b> <sup>8</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	trace
10	<b>L</b> <sup>9</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	trace
11	<b>L</b> <sup>10</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	trace
12	<b>L</b> <sup>5</sup>	none	acetone	0
13 <sup>b</sup>	<b>L</b> <sup>5</sup>	Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	acetone	99
14	/	<b>1</b> (1 mol%)	acetone	99

<sup>a</sup> General reaction conditions: **2a** (0.5 mmol), ligand (10 mol%), manganese salt (5 mol%), solvent (2 mL), room temperature in a reaction tube without nitrogen protection, 1 h, GC yield; **4a** was not observed in all the reactions; <sup>b</sup> **L**<sup>5</sup> (2 mol%), Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mol%).



Reacting **L**<sup>5</sup> with Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O led to the complex **1**. The structure of **1** has been determined by X-ray diffraction and shows a severely distorted octahedral geometry (Scheme 2; see SI for more details). The isolated **1** displayed a similar activity as that prepared in situ (entries 13 and 14, Table 1). Further screening led to the optimized oxidation conditions, i.e. **1** (1 mol%) being the catalyst and H<sub>2</sub>O<sub>2</sub> (2.5 equiv.) as the oxidant in acetone at room temperature (Table A, SI). Under such neutral

conditions, **2a** was oxidized to **3a** with high yield and *no formation of any disiloxane byproduct* (entry 14, Table 1). It is noted that compared with the literature reports on manganese-catalyzed oxidation reactions, acid or base additives suppressed, instead of promoting, the oxidation in question (Table B, SI).<sup>[12]</sup>



**Scheme 2.** Formation of **1** and its molecular structure determined by single-crystal X-ray diffraction. Selected bond distances: Mn01–N1, 2.179(4) Å; Mn01–N2, 2.182(4) Å; Mn01–O6, 2.125(6) Å; Mn01–O7, 2.050(5) Å. Selected bond angles: N1–Mn01–N1a, 117.8(2)°; N1–Mn01–N2a, 100.47(16)°; N1–Mn01–N2, 74.24(16)°; N2–Mn01–N2a, 170.0(2)°.

**Table 2.** Scope of **1**-catalyzed oxidation of hydrosilanes<sup>a</sup>

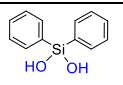
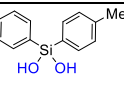
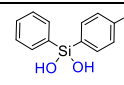
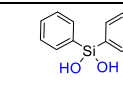
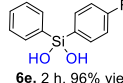
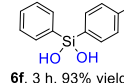
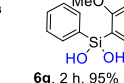
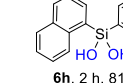
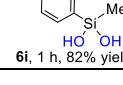
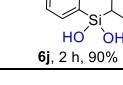
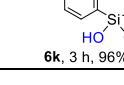
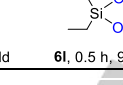
$\begin{array}{c} R^1 \\   \\ ^2R-Si-H \\   \\ R^3 \end{array} \xrightarrow[H_2O_2 (2.5 \text{ equiv.}), \text{acetone}]{\textbf{1} (1 \text{ mol\%})} \begin{array}{c} R^1 \\   \\ ^2R-Si-OH \\   \\ R^3 \end{array}$			
<b>3a</b> , 0.25 h, 97% yield	<b>3b</b> , 0.25 h, 97% yield	<b>3c</b> , 0.25 h, 96%	<b>3d</b> , 0.25 h, 93% yield
<b>3e</b> , 0.25 h, 94% yield	<b>3f</b> , 0.25 h, 95% yield	<b>3g</b> , 0.25 h, 94% yield	<b>3h</b> , 0.25 h, 94% yield
<b>3i</b> , 0.25 h, 97% yield	<b>3j</b> , 0.25 h, 91% yield	<b>3k</b> , 1 h, 91% yield	<b>3l</b> , 0.25 h, 95% yield
<b>3m</b> , 1 h, 85% yield	<b>3n</b> , 0.25 h, 95% yield	<b>3o</b> , 0.25 h, 94% yield	<b>3p</b> , 0.25 h, 96% yield
<b>3q</b> , 0.25 h, 75% yield	<b>3r</b> , 0.25 h, 93% yield	<b>3s</b> , 2 h, 80% yield	<b>3t</b> , 0.25 h, 98% yield

<sup>a</sup> General reaction conditions: **2** (0.5 mmol), catalyst **1** (1 mol %), solvent (2 mL), room temperature in a reaction tube without nitrogen protection, isolated yield.

Under the optimized conditions, the catalytic system proved to be generally effective for the selective oxidation of various hydrosilanes to silanols in a short time (Table 2). Thus, the protocol was shown to tolerate sterically varied substituents in substrates **2a–2c**, affording the corresponding silanols **3a–3c** in high yields without byproduct formation. Both electron-donating and electron-withdrawing phenyl substituents are suitable, leading to the silanol products with excellent isolated yields

(Table 2, **3d-3j**). Replacing the phenyl with 2-naphthyl did not affect the efficacy of the catalysis; but the sterically hindered 1-naphthyl necessitated a longer time of 1 h to complete (**3k** vs **3l**). A heterocyclic thiofuran-substituted silanol was also obtained in good yield in 1 h (**3m**), so were the benzyl and alkyl substituted silanols (**3n-3q**). Notably, the substrate **2r** with an alkynyl functional group was well tolerated under the oxidation conditions, affording the silanol **3r** in 93% yield. However, for the substrate **2s** which contains a 4-vinyl substituent, both the hydride and C=C double bond were oxidized, affording the silanol **3s** under the standard conditions. Furthermore, the substrate **2t** with two Si-H groups was completely oxidized to a silandiol in excellent yield (**3t**). The silanol **3s** with an epoxide and **3t** with two Si-OH functional groups could be used as building blocks for material synthesis.

**Table 3.** Scope of **1**-catalyzed oxidation of dihydrosilanes<sup>a</sup>

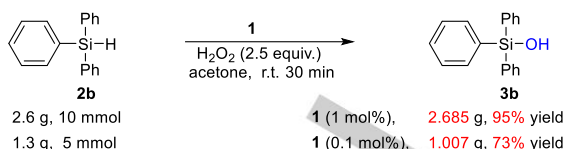
$\begin{array}{c} \text{R}^1 \\   \\ \text{R}-\text{Si}-\text{H} \\   \\ \text{H} \\ \mathbf{5} \end{array} \xrightarrow[\text{H}_2\text{O}_2 \text{ (5 equiv.), acetone}]{\mathbf{1} \text{ (2 mol\%)}} \begin{array}{c} \text{R}^1 \\   \\ \text{R}-\text{Si}-\text{OH} \\   \\ \text{OH} \\ \mathbf{6} \end{array}$	
 <b>6a</b> , 1 h, 94% yield	 <b>6b</b> , 2 h, 93% yield
 <b>6c</b> , 3 h, 95% yield	 <b>6d</b> , 2 h, 95% yield
 <b>6e</b> , 2 h, 96% yield	 <b>6f</b> , 3 h, 93% yield
 <b>6g</b> , 2 h, 95% yield	 <b>6h</b> , 2 h, 81% yield
 <b>6i</b> , 1 h, 82% yield	 <b>6j</b> , 2 h, 90% yield
 <b>6k</b> , 3 h, 96% yield	 <b>6l</b> , 0.5 h, 92% yield

<sup>a</sup> General reaction conditions: **5** (0.5 mmol), catalyst **1** (2 mol %), solvent (2 mL), room temperature in a reaction tube without nitrogen protection, isolated yield.

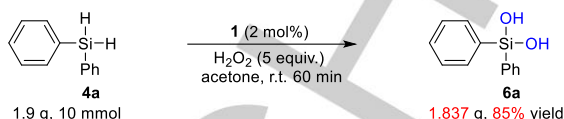
Geminal silandiols have found applications in silicon-based materials,<sup>[1,2]</sup> drugs,<sup>[1,3]</sup> and organocatalysis<sup>[1,6]</sup> (Figure S1, SI). However, the synthesis of silandiols via transition metal-catalyzed oxidation of dihydrosilanes is usually more difficult than that of silanols, because of the formation of disiloxanes and incomplete oxidation products.<sup>[8-10]</sup> Our catalytic system is effective, allowing for the oxidation of various substituted dihydrosilanes to silandiols. Thus, under the catalysis of **1** (2 mol%) with H<sub>2</sub>O<sub>2</sub> (5 equiv.) as oxidant in acetone, dihydrodiphenylsilane **5a** was oxidized to the silandiol **6a** in 94% isolated yield in 1 h reaction time (Table 3, **6a**). Both electron-donating and electron-withdrawing aryl substituents are suitable, furnishing the silandiol products with excellent isolated yields with no disiloxane formation (Table 3, **6b-6h**). Replacing one of the aryl substituents with an alkyl one did not significantly affect the product yields (Table 3, **6i-6k**). Oxidation of the less bulky dihydro diethylsilane **5l** led to the silandiol **6l**, which has been used as an organocatalyst for 1,4-addition reactions.<sup>[6]</sup>

To further demonstrate the synthetic utility of the **1**-catalyzed oxidation of organosilanes, the bulky triphenylsilane **2b** and diphenylsilane **4a** were subjected to a gram-scale reaction. As shown in Scheme 3, the corresponding silanols **3b** and **6a** were obtained in excellent yield. Notably, this gram-scale oxidation could be performed at a lower catalyst loading of 0.1 mol%, as showcased by the conversion of **2b** to **3b**.

a) Catalytic oxidation of hydrosilane of **2b** on gram scale



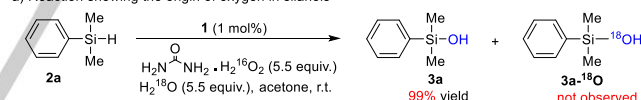
b) Catalytic oxidation of dihydrosilane of **4a** on gram scale



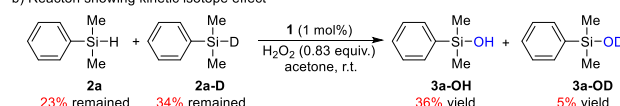
**Scheme 3.** Gram-scale oxidation of hydrosilanes.

To gain insight into the oxidation mechanism, a few experiments were performed. In the absence of H<sub>2</sub>O<sub>2</sub> but with the reaction opened to the air, the model substrate **2a** did not undergo any oxidation in the presence of **1**, with or without water (Table B, SI). Introducing H<sub>2</sub><sup>18</sup>O (5.5 equiv.) to the reaction under the standard conditions, **3a** was obtained in 99% yield; but no <sup>18</sup>O-labeled silanol was observed by HRMS analysis (Scheme 4, a). These observations indicate that molecular oxygen or water is not the oxygen source of the silanol product. A small but significant kinetic isotope effect, comparable to that observed in the polyoxotungstate-catalyzed oxidation of hydrosilanes,<sup>[10f]</sup> could be seen in the oxidation of **2a** vs that of **2a-D** (Scheme 4, b),<sup>[14]</sup> suggestive of the involvement of Si-H bond scission in the turnover limiting step. To detect possible intermediate silane species, the oxidation of **2b** under the standard conditions was monitored with in situ IR spectroscopy by following the absorption at ν<sub>Si-H</sub> = 806 cm<sup>-1</sup> and ν<sub>Si-OH</sub> = 874 cm<sup>-1</sup>. The result indicates the oxidation to be complete in 20 min, with no other silane species being accumulated during the oxidation (Figure S1, SI).

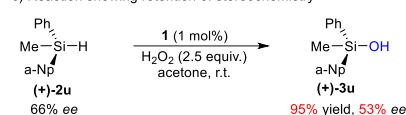
a) Reaction showing the origin of oxygen in silanols



b) Reaction showing kinetic isotope effect



c) Reaction showing retention of stereochemistry



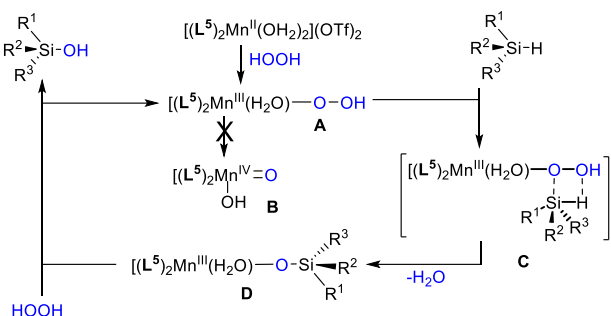
**Scheme 4.** Reactions aimed to probe the oxidation mechanism.

A more revealing experiment is the oxidation of an optically active hydrosilane (+)-**2u** (66% ee) with H<sub>2</sub>O<sub>2</sub> under the catalysis of **1** (Scheme 4, c). The reaction proceeded selectively to afford the corresponding silanol (+)-**3u** in 95% isolated yield and 53% ee. Note the high-degree retention of the configuration of silicon; this suggests that the oxidation in question may not involve hetero- or homo-lysis of the Si-H bond before the formation of the silanol; rather it may proceed via a concerted process.<sup>[8,10c,10d,10f]</sup>

Considering the observations above, we propose the following catalytic cycle for the oxidation catalyzed by **1** (Scheme 5). Initially, **1** reacts with H<sub>2</sub>O<sub>2</sub> to form the active



hydroperoxide **A**. Although highly active manganese oxo species could be formed from **A** in the presence of an acid or water, the suppressing effect of acid on the oxidation (Table B, SI) and the lack of  $^{18}\text{O}$  incorporation from  $\text{H}_2^{18}\text{O}$  mentioned above indicate that a species, such as **B**, is not involved in the oxidation.<sup>[15]</sup> Instead, **A** might react directly with the hydrosilane via a transition state **C** involving concerted transfer of the silicon and hydride to the electrophilic hydroperoxide moiety of the manganese species to afford the siloxide **D**.<sup>[15,16]</sup> Protonation of **D** by  $\text{H}_2\text{O}_2$  then generates the silanol product and the active intermediate **A**, restarting the catalysis.



**Scheme 5.** Proposed mechanism for the **1**-catalyzed oxidation of hydrosilanes.

In conclusion, by harnessing the remarkable catalytic activity of the electron-rich manganese complex **1**, we have realized the highly efficient oxidation of organosilanes to silanols with  $\text{H}_2\text{O}_2$  under neutral conditions. A series of hydrosilanes and dihydrosilanes were oxidized to silanols and silandriols, respectively, with excellent isolated yields and no waste byproduct formation in a short reaction time. Preliminary mechanistic studies suggest that the oxidation may proceed via a concert reaction of a  $\text{Mn}(\text{III})$ -OOH species with the hydrosilane. Further investigation is in progress.

## Acknowledgements

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**Keywords:** silanols • silandriols • hydrosilanes • catalytic oxidation • manganese complex

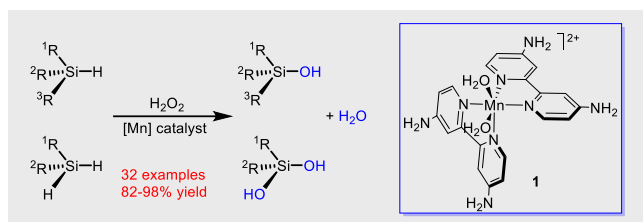
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- [14] The KIE may be estimated from the remaining **2a** and **2a-D**. The low yield of **3a-OD** is due to H-D exchange with water in the system.
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- [16] Following the suggestion of a reviewer, we also carried out the 1-catalyzed oxidation of **2a** using the single oxygen atom donors  $\text{tBuOOH}$ ,  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  and  $\text{PhIO}$  under the optimized conditions (Table 1). The former two oxidants afforded 99% yield (GC) of **3a**; but no oxidation was observed with  $\text{PhIO}$  (Table B, SI). These results appear to be supportive of the concerned mechanism suggested.

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Manganese Catalyzed Highly Selective Oxidation of Hydrosilanes to Silanols under Neutral Conditions



A manganese complex catalyzes the chemoselective oxidation of hydrosilanes and dihydrosilanes with  $H_2O_2$  to afford various silanols and silandiols, with the selectivity controlled solely by the catalyst **1**.